THE STRUCTURE OF BENZOPYRYLIUM SALTS

BY

A. VERN McINTOSH, JR.

B.S., Kent State University, 1938

M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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A. THE STRUCTURE OF THE BENZOPYRLIUM ION

Introduction

The benzopyrylium ion contains a benzene ring fused to a pyrane ring. In the possible structures that may be written for the ion, the positive charge may be placed only on the heterocyclic oxygen atom or on the 2- or 4-carbon atoms. In the carbonium ion structures, if the positive charge is on the 2-carbon atom a double bond exists between the 3- and 4-carbon atoms, while if the charge is on the 4-carbon atom the double bond must be between the 2- and 3-carbon atoms. The carbonium ions may change from one form to the other by an allylic shift involving the rearrangement of an electron pair. One object of this thesis was to determine whether the benzopyrylium ion was an oxonium or a carbonium ion and, if a carbonium ion, whether the positive charge lay on the 2- or the 4-carbon atom.

Theoretical and Discussion of Results

Lines of evidence discussed in the literature were reviewed. It was found that evidence based on synthesis was invalid. The benzopyrylium salts produced by reactions which should result in the formation of carbonium ions with the charge on the 2-carbon atom were identical with salts which were produced by reactions which should have given the isomeric structures with the charge on the 4-carbon atom. An allylic rearrangement occurred.

Shriner and Moffett[1] subjected several benzopyrylium salts to ozonization. The results showed that in each salt double bonds were present between the 2,3- and 3,4-carbon atoms. This indicated that the carbonium forms were present in equilibrium. Löwenbein[2] showed that when benzopyrylium salts were treated with Grignard reagents a simple coupling reaction occurred, in which the R group of RMgX became

attached to either the 2- or the 4-carbon atom. These results supported both carbonium ion structures. In hydrolysis and alcoholysis of benzopyrylium salts the hydroxyl or alkoxyl group has always been found attached to the 2-carbon atom. This indicated that the 2-carbon atom was positive. Moffett[3] found that the orientation of the entering substituent in the nitration of 2,3-diphenylbenzopyrylium salts indicated that the 2-carbon atom was positive.

In this investigation, ozonization of 2,3-diphenyl-4-(*p*-anisyl)-6-methylbenzopyrylium perchlorate was attempted. The compound was found to be highly resistant to ozonization.

2,3-Diphenyl-4-(*p*-anisyl)-6-methylbenzopyrylium perchlorate and the corresponding ferrichloride were found to be strong electrolytes in nitrobenzene solution. The conductivity curves of these compounds were quite similar to that of tri-*p*-anisylcarbonium perchlorate. The apparent molecular weights of the above compounds measured in nitrobenzene solution at the freezing point were slightly over half the calculated value, indicating high ionization. These analogous properties of benzopyrylium and carbonium ions lend support to the carbonium ion structures.

The absorption spectra of 2,3-diphenyl-4-(*p*-anisyl)-6-methylbenzopyrylium perchlorate (I), 2-(*p*-anisyl)-3-phenyl-4-(*p*-tolyl)-6-methylbenzopyrylium perchlorate (II), 9-(*p*-anisyl)-xanthylium perchlorate (III) and 2-(*p*-anisyl)-3,4,5,6-dibenzopyrylium perchlorate (IV) were measured in the visible region. The spectra of compounds II and IV were much more similar than the spectra of compounds I and III. Since in compound IV the double bond should be frozen in a position corresponding to the 3,4-position in benzopyrylium salts, this constitutes further evidence that the positive charge is on the 2-carbon atom.

In summary, all the evidence indicates that the benzopyrylium ions are carbonium ions, and it is probable that the positive charge is on the 2-carbon atom.

B. THE STRUCTURE OF BENZOPYRYLIUM COMPOUNDS IN NEUTRAL SOLUTION

Buck and Heilbron[4] postulated that on neutralization of a solution containing 4′-hydroxyflavylium chloride the salt lost hydrogen chloride and assumed a quinoid structure. In this research an attempt was made to prove this hypothesis. Following the procedure of Irvine and Robinson[5] the "color base" produced from 4′-hydroxyflavylium chloride by treatment with aqueous sodium acetate was isolated. It could not be purified. The absorption spectrum of the isolated "color base" in benzene solution was sufficiently similar to the absorption spectrum of 4′-hydroxyflavylium chloride in aqueous solution at *p*H 8.03 to show that the "color base" was actually the compound responsible for the red color of the aqueous solution.

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VITA

The author was born in Chardon, Ohio, on May 25th, 1917. He attended grammar school in Chardon and in Claridon, Ohio. He graduated from Chardon High School in June, 1934. Entering Kent State University in September, 1935, he graduated in June, 1938, with the B. S. degree. He entered the University of Illinois in September, 1938, and received the M. S. degree in June, 1939. From July, 1939, to September, 1940, he worked as research chemist at the Lake Erie Chemical Company, Cleveland, Ohio, then returned in September, 1940, to the University of Illinois for graduate study.

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